

Flash Photolysis Study of Sulfite, Thiocyanate, and Thiosulfate Ions in Solution

TECHNICAL REPORT
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The primary photolytic processes, as observed by the technique of flash photolysis, were studied for the sulfur polyvalent anions SO_3^{2-} , CNS^- , and $\text{S}_2\text{O}_3^{2-}$ in aqueous solution. Sulfite ions were found to produce two transient species, resulting from the primary photolytic process: $\text{SO}_3^{2-} \cdot \text{H}_2\text{O} \xrightarrow{h\nu} \text{SO}_3^- + e_{aq}^-$. A short-lived species apparently formed by the addition of e_{aq}^- to sulfite ions and tentatively assigned to HSO_3^{2-} ($\lambda_{\text{max}} 720 \text{ m}\mu$) decays by first-order process, $k = (1.9 \pm 0.3) \times 10^4 \text{ sec}^{-1}$, and a longer lived species assigned to SO_3^- ($\lambda_{\text{max}} \sim 275 \text{ m}\mu$) decays by second-order process, $2k/\epsilon = 1.5 \times 10^6$ at $275 \text{ m}\mu$. Thiocyanate ions decompose on photolysis by at least two processes: $\text{CNS}^- \cdot \text{H}_2\text{O} \xrightarrow{h\nu} \text{CNS} + e_{aq}^-$ and $\text{CNS}^- \xrightarrow{h\nu} \text{CN}^- + \text{S}$. A transient spectrum, due to $(\text{CNS})_2^-$ radical anions, was found absorbing at $\lambda_{\text{max}} 485 \text{ m}\mu$, with species decaying by a first-order process in air-free solutions and by a second-order process in the presence of oxygen. Thiosulfate ions decompose on photolysis by two processes: $\text{S}_2\text{O}_3^{2-} \cdot \text{H}_2\text{O} \xrightarrow{h\nu} \text{S}_2\text{O}_3^- + e_{aq}^-$ and $\text{S}_2\text{O}_3^{2-} \cdot \text{H}_2\text{O} \xrightarrow{h\nu} \text{S}_2\text{O}_2^- + \text{OH}^- + \text{OH}^-$. The OH radicals produced react with $\text{S}_2\text{O}_3^{2-}$ to form S_2O_3^- radicals. A transient optical spectrum with a $\lambda_{\text{max}} 380 \text{ m}\mu$ assigned to S_2O_3^- decays by a second-order process in the absence of O_2 and by a first-order process in the presence of O_2 . S_2O_2^- has a $\lambda_{\text{max}} \sim 280 \text{ m}\mu$ and decays by a second-order process in the presence or absence of oxygen. The CTTS absorption bands of the three sulfur anions have been determined. The esr spectra of the radicals produced on uv irradiation of SO_3^{2-} , CNS^- , and $\text{S}_2\text{O}_3^{2-}$ ices at 77°K are given.

The ultraviolet absorption spectra of the sulfur polyvalent anions SO_3^{2-} , CNS^- , and $\text{S}_2\text{O}_3^{2-}$ are known, but, except for thiosulfate anions, their absorption spectra have not been characterized and their photochemistry has not been studied for many years.

Albu and Goldfinger¹ examined the absorption spectrum of the sulfite ion on the basis of the Franck-Haber theory of the electron-affinity spectrum of ions and showed that the SO_3^{2-} spectrum has a long wavelength limit of 2660 \AA and corresponds to the process $\text{SO}_3^{2-} \cdot \text{H}_2\text{O} \xrightarrow{h\nu} \text{SO}_3^- + \text{H} + \text{OH}^-$. Haber and Wansbrough-Jones² studied the photochemistry of sulfite ions in the absence of oxygen and postulated the reactions $\text{H} + \text{H} \rightarrow \text{H}_2$ and $\text{SO}_3^- + \text{SO}_3^- \rightarrow \text{S}_2\text{O}_6^{2-}$ taking place under their experimental conditions. However, they found the quantum yield of dithionate to be 0.07 at pH 7.0 and suggested the possibility of the "back reaction" $\text{SO}_3^- + \text{H} \rightarrow \text{HSO}_3^-$ occurring. Bäckström³ studied the effects of inhibitors, particularly alcohols, on the photochemical oxidation of sulfite ions in solution.

Thiocyanate ions were found⁴ to decompose with light in the wavelength range $1800\text{--}3000 \text{ \AA}$ with the formation of sulfur. The reaction was postulated to be reversed in the dark. Matheson, *et al.*,⁵ found evidence for the formation of solvated electrons in the flash photolysis of aqueous solutions of CNS^- ions, and Gusarsky and Treinin⁶ interpreted the absorption band of thiocyanate ions at $\sim 220 \text{ m}\mu$ as due to a charge-transfer-to-solvent (CTTS) spectra.

The spectrum of $\text{S}_2\text{O}_3^{2-}$ in solution has an intense absorption peak at about $215 \text{ m}\mu$,^{7,8} and has been assigned to a CTTS type of excitation.⁸⁻¹⁰ The limiting (maximum) quantum yield of decomposition of the CTTS band was found¹⁰ to be <0.1 in the presence of electron scavengers in solution.

In this work, the results on the flash-photolysis study of sulfite, thiocyanate, and thiosulfate anions in aqueous solution is presented. The primary photochemical processes occurring in these systems are discussed and the optical absorption spectra of the short-lived transients are identified.

Experimental Section

The flash-photolysis lamps and setup used in this work have been described elsewhere.¹¹ Total flash

- (1) H. W. Albu and P. Goldfinger, *Z. Phys. Chem.*, **16B**, 338 (1932).
- (2) F. Haber and O. H. Wansbrough-Jones, *ibid.*, **18B**, 103 (1932).
- (3) H. Bäckström, *J. Amer. Chem. Soc.*, **49**, 1460 (1927); *Z. Phys. Chem.*, **25B**, 122 (1934).
- (4) K. Jablczyński and H. Jablczyńska, *Rocz. Chem.*, **10**, 579 (1930); *Bull. Soc. Chim. France*, **49**, 877 (1931).
- (5) M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, **67**, 2613 (1963).
- (6) E. Gusarsky and A. Treinin, *ibid.*, **69**, 3176 (1965).
- (7) A. D. Autrey and R. E. Connick, *J. Amer. Chem. Soc.*, **73**, 1842 (1951).
- (8) M. Smith and M. C. R. Symons, *J. Chem. Phys.*, **25**, 1074 (1956).
- (9) D. P. Ames and J. Willard, *J. Amer. Chem. Soc.*, **75**, 3267 (1953); W. S. Fyfe, *J. Chem. Phys.*, **37**, 1894 (1962).
- (10) R. Sperling and A. Treinin, *J. Phys. Chem.*, **68**, 897 (1964).

energies of 1800 J were used with a duration at "1/e time" of 5 μsec and a total flash duration of 70 μsec . A Bausch and Lomb grating monochromator with gratings blazed in the uv, visible, and near-ir regions were used. An EMI 9558QB photomultiplier tube was employed throughout this work. The optical absorption spectra of the transient species produced were obtained by the point-by-point method.

Solutions were prepared just previous to irradiation using water purified by triple distillation, radiolysis, and photolysis.¹² Reagents used were the best research grade supplied by Baker and Adamson and Mallinckrodt, and they were used without further

Results and Discussion

Photolysis of Sulfite Ions. All the work reported below was carried out in $10^{-2} M$ Na_2SO_3 solutions. The flash photolysis of sodium sulfite in aqueous solution gave rise to the formation of a transient species absorbing strongly in the wavelength region 350–1000 $m\mu$, see Figure 1, with a λ_{max} at about 720 $m\mu$. Except for variations in the amount of transient produced, the same optical spectrum was obtained at all sulfite ion concentrations studied up to $10^{-1} M$. Similarly, the same transient was formed in the presence or absence of oxygen (Figure 1). This broad absorption spectrum, with a peak at about 720 $m\mu$, was found to be due to

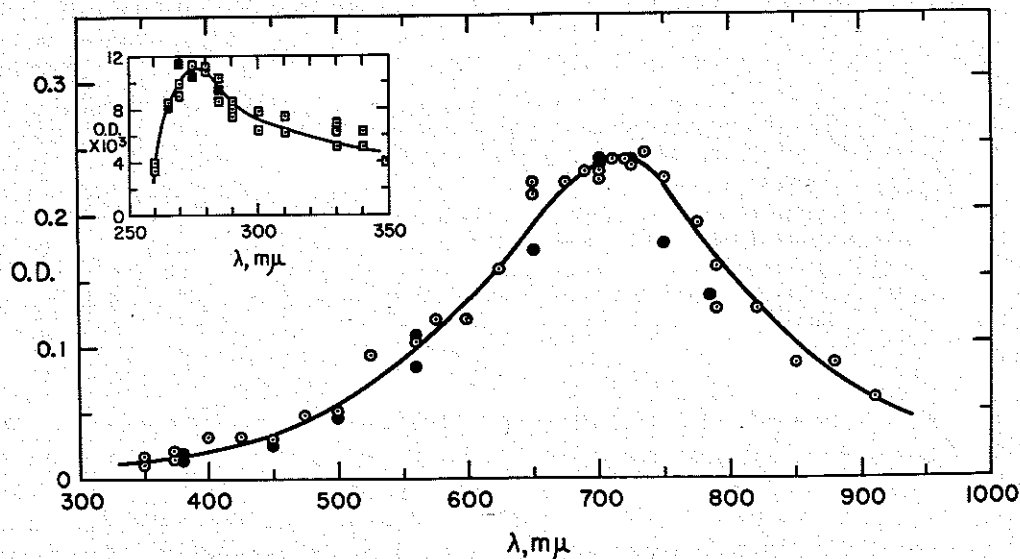


Figure 1. Transient absorption spectra produced on flash photolysis of $10^{-2} M$ Na_2SO_3 at pH 6.0, in N_2 -saturated (\odot) and in air-saturated (\bullet) solution. Optical density measured in 20-cm optical cells, 25 μsec after start of flash. Inset: longer lived transient measured in N_2 -saturated (\square) and air-saturated (\blacksquare) solutions 300 μsec after start of flash.

purification. Solutions were deaerated, using pre-purified nitrogen, by the syringe technique or by using a bubbler with a wide glass frit at the bottom of a cylindrical vessel under continuous N_2 gas flow conditions. The concentration of the solutes used in this investigation was kept to a minimum to reduce "inner-filter" effects but sufficient to obtain enough transient. Furthermore, since sulfur was produced in the photolysis of the three anions studied, it was essential to keep its concentration down to a minimum to avoid interference with the transmission of the monitoring light beam through the optical cell.

The esr spectra were recorded with a Varian V-4500 X-band spectrometer with 100-kc/sec modulation and a 9-in. electromagnet equipped with the Fielddial. A dual cavity was usually used together with a double recorder. The irradiated sample was placed in one cavity and in the other a KCl-pitch sample was used. All spectra were measured at 77°K, even those that were annealed at higher temperatures.

one single species which decays by a first-order process (see Table I). The decay rate of the transient was found to be the same in the presence or absence of oxygen, in neutral solution or at pH 12.0, with an average decay constant $k = 1.9 \pm (0.3 \times 10^4) \text{ sec}^{-1}$. On flashing a $10^{-2} M$ Na_2SO_3 solution saturated with N_2O gas, no transient was found absorbing in the wavelength region 500–800 $m\mu$.

A second transient species was observed on photolysis of $10^{-2} M$ SO_3^{2-} ions in N_2 , N_2O , and air-saturated solutions, absorbing in the wavelength region 250–380 $m\mu$, with a maximum absorption peak at about 275 $m\mu$; see Figure 1. This intermediate absorbs considerably less than the species with λ_{max} 720 $m\mu$, is longer lived, with a half-life of a few milliseconds, and decays by a second-order process; see Table I.

(11) L. Dogliotti and E. Hayon, *J. Phys. Chem.*, **71**, 2511 (1967).
M. Langmuir and E. Hayon, *ibid.*, **71**, 3808 (1967).

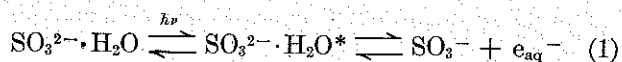
(12) E. Hayon, *Trans. Faraday Soc.*, **60**, 1059 (1964).

Table I: Rate Constants for the Decay of Transients Produced on Flash Photolysis of $10^{-2} M$ Na_2SO_3

Transient	System	pH	λ , $m\mu$	Decay rate ^a
HSO_3^{2-}	N_2 satd	Neutral	375	$k = 2.0 \times 10^4 \text{ sec}^{-1}$
HSO_3^{2-}	N_2 satd	Neutral	575	$k = 1.7 \times 10^4 \text{ sec}^{-1}$
HSO_3^{2-}	N_2 satd	Neutral	675	$k = 1.8 \times 10^4 \text{ sec}^{-1}$
HSO_3^{2-}	N_2 satd	Neutral	700	$k = 1.9 \times 10^4 \text{ sec}^{-1}$
HSO_3^{2-}	Air satd	Neutral	375	$k = 2.0 \times 10^4 \text{ sec}^{-1}$
HSO_3^{2-}	Air satd	Neutral	650	$k = 2.1 \times 10^4 \text{ sec}^{-1}$
HSO_3^{2-}	Air satd	Neutral	675	$k = 1.7 \times 10^4 \text{ sec}^{-1}$
HSO_3^{2-}	N_2 satd	11.9	650	$k = 1.4 \times 10^4 \text{ sec}^{-1}$
HSO_3^{2-}	$5 \times 10^{-4} M$ ethanol, air satd	Neutral	650	$k = 2.2 \times 10^4 \text{ sec}^{-1}$
SO_3^-	N_2 satd	Neutral	275	$2k/\epsilon = 1.5 \times 10^6$
SO_3^-	N_2 satd	Neutral	280	$2k/\epsilon = 1.5 \times 10^6$
SO_3^-	N_2 satd	Neutral	290	$2k/\epsilon = 1.6 \times 10^6$
SO_3^-	Air satd	Neutral	270	$2k/\epsilon = 1.7 \times 10^6$
SO_3^-	Air satd	Neutral	275	$2k/\epsilon = 1.3 \times 10^6$
SO_3^-	Air satd	Neutral	280	$2k/\epsilon = 1.9 \times 10^6$

^a Deviation is $\pm 15\%$.

The above experimental observations are explained on the basis that the main primary photolytic process resulting from the absorption of light by SO_3^{2-} ions is due to a CTTS transition, leading to the formation of SO_3^- radical anions and solvated electrons, according to

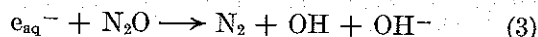


While the release of electrons from the spectroscopic excited state of sulfite ions can account and explain the results obtained by this flash-photolysis technique, one cannot exclude other photolytic processes which may be occurring simultaneously but which do not give rise to observable absorbing species under the conditions of our experiments. This is also true of the other systems described below.

The electron released in reaction 1 is considered to form an adduct with sulfite ions, giving an intermediate which is tentatively assigned to HSO_3^{2-}



The species with $\lambda_{\text{max}} 720 m\mu$ is assigned to the HSO_3^{2-} radical anion and the species with $\lambda_{\text{max}} \sim 275 m\mu$ is assigned to the SO_3^- radical anion. These assignments have been made taking into consideration the following facts and observations. The HSO_3^{2-} transient with $\lambda_{\text{max}} 720 m\mu$ is not formed on photolysis of SO_3^{2-} in presence of $2 \times 10^{-2} M$ N_2O . This is explained on the basis of a kinetic competition between reaction 2 and



with $k_3 = 5.6 \times 10^9 M^{-1} \text{ sec}^{-1}$.¹³ Under these experimental conditions ($10^{-2} M$ SO_3^{2-} and $2 \times 10^{-2} M$ N_2O at neutral pH), all the electrons have reacted

with N_2O according to reaction 3. The slow-decaying transient absorbing with $\lambda_{\text{max}} \sim 275 m\mu$ was still observed in N_2O solutions, indicating that e_{aq}^- is not involved in its formation.

Addition of H^+ ions, to convert e_{aq}^- to H atoms, where $k_4 = 2.3 \times 10^{10} M^{-1} \text{ sec}^{-1}$ ¹³ was found



not to be feasible. Franck-Haber's theory predicts that the corresponding electron-affinity spectrum of the bisulfite ion should be 1.5–2.0 eV to the shorter wavelength side of that of the sulfite ion. In agreement with this prediction, no absorption by the bisulfite ion was found at $\lambda > 2250 \text{ \AA}$, and no transient species were produced on flash photolysis of $10^{-2} M$ sodium bisulfite or $10^{-2} M$ sodium sulfite at pH 1.1–2.0, in air or N_2 -saturated solutions.

Instead of using H^+ ions as an electron scavenger, nitrate ions were added to a $10^{-2} M$ SO_3^{2-} solution. In N_2 -saturated solution containing $2 \times 10^{-4} M$ KNO_3 , no transient was observed at $720 m\mu$. However, using lower concentrations of NO_3^- ions, it was possible to form some HSO_3^{2-} and observe its decay. At $720 m\mu$, the transient was found to decay by a pseudo-first-order process dependent on $[\text{NO}_3^-]$, from which a $k(\text{HSO}_3^{2-} + \text{NO}_3^-) \simeq 10^9 M^{-1} \text{ sec}^{-1}$ was calculated. In addition, from the competition between reaction 2 and $k(e_{\text{aq}}^- + \text{NO}_3^-)$, it was estimated that $k(e_{\text{aq}}^- + \text{SO}_3^{2-}) \leq 2 \times 10^6 M^{-1} \text{ sec}^{-1}$.

Pulse radiolysis of aqueous solutions of sulfite ions was examined by Adams, *et al.*^{14,15} In a first pub-

(13) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967).

(14) G. E. Adams, J. W. Boag, and B. D. Michael, *Proc. Chem. Soc.*, 411 (1964).

lication¹⁴ a transient spectrum with $\lambda_{\text{max}} \approx 350 \text{ m}\mu$ was reported on irradiation of neutral aqueous solutions in the presence of oxygen. This spectrum was suggested to be formed from the reaction $\text{OH} + \text{SO}_3^{2-} \rightarrow \text{SO}_3^- + \text{OH}^-$ and was assigned to the SO_3^- radical. In a later work, Adams, *et al.*,¹⁵ found no transient on pulse radiolysis of 0.5 M sulfite ions in presence of $2 \times 10^{-2} \text{ M}$ N_2O gas. In the presence of oxygen, they now observed a transient with an absorption maximum at $750 \text{ m}\mu$ but with no transient peaking at $\sim 350 \text{ m}\mu$, indicating that the transient has a reducing species (e_{aq}^- or O_2^-) as a precursor.

Their later results¹⁵ are in accord with the results presented above for the species absorbing at $720 \text{ m}\mu$ in the flash photolysis of SO_3^{2-} ions. The difference in λ_{max} is thought to be due to the use¹⁵ of flash spectrography in deriving the absorption spectrum of the transient.

Since $k(\text{e}^- + \text{O}_2 \rightarrow \text{O}_2^-) = 1.9 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ and $k(\text{e}^- + \text{SO}_3^{2-})$ was estimated as $\leq 2 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$, all the electrons produced in reaction 1 must react with oxygen under the experimental conditions described above. The formation of the transient on photolysis of air-saturated solutions is then probably the result of the reaction $\text{O}_2^- + \text{SO}_3^{2-} \xrightarrow{\text{H}_2\text{O}} \text{HSO}_3^- + \text{OH}^- + \text{O}_2$.

The assignment of the slow-decay species, with $\lambda_{\text{max}} \sim 275 \text{ m}\mu$, to the SO_3^- radical anion was based on the following premises. Since the transient with $\lambda_{\text{max}} 720 \text{ m}\mu$ is formed as the result of the reaction of e_{aq}^- with SO_3^{2-} , the SO_3^- radical produced in the primary photolytic process could well account for the observed absorption spectrum in the uv region. In addition, the OD at $270 \text{ m}\mu$ was found to increase from 0.012 to 0.025 in air- or N_2 -saturated solutions compared to N_2O -saturated solutions. This doubling of the amount of SO_3^- radical formed is explained on the basis of reaction 3 followed by $\text{OH} + \text{SO}_3^{2-} \rightarrow \text{SO}_3^- + \text{OH}^-$. This observation provides strong support for the proposed main primary process taking place in the photolysis of sulfite ions, *viz.* reaction 1.

The examination¹⁶ of the esr spectrum produced on uv irradiation of 10^{-2} M Na_2SO_3 ices at 77°K showed a singlet with an isotropic g factor very close to 2.000 (see Figure 2a). The sulfite ice was colorless after uv irradiation, and the esr single line was found to disappear on thermal annealing of the ice to about -70° . Chantry, *et al.*,¹⁷ have observed the optical and esr spectra of SO_3^- radicals produced on γ irradiation of single crystals of sodium dithionite, sulfamic acid, and potassium sulfamate. The esr spectrum reported¹⁷ is a single line with an isotropic g factor of 2.004 due to $^{32}\text{SO}_3^-$ radicals. They also found a uv absorption at 270 and $240 \text{ m}\mu$ and concluded that the $270\text{-m}\mu$ band is due to SO_3^- radicals. More recently, Gromov and Morton¹⁸ have observed the esr spectrum of SO_3^-

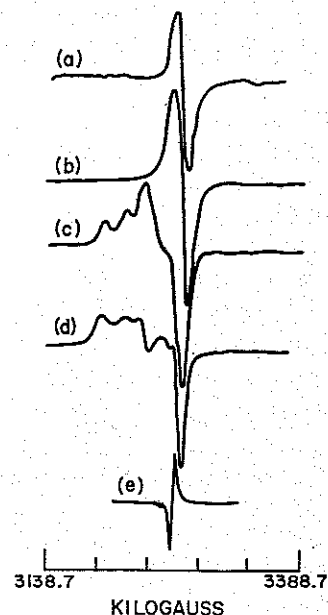


Figure 2. Electron spin resonance spectra of trapped radicals produced on uv irradiation at 77°K : (a) 10^{-2} M Na_2SO_3 , colorless, radical disappears at -70° ; (b) 10^{-2} M NaHSO_3 , purple-violet, radical and color disappear at -75° ; (c) 10^{-2} M KCNS , red, radical and color disappear at -95° ; (d) 10^{-2} M $\text{Na}_2\text{S}_2\text{O}_3$, yellow, radical and color disappear at -60° ; (e) pitch sample.

formed from γ irradiation of K_2SO_4 crystals and found the principal values of the g tensors of the radical to be in good agreement with those reported by Chantry, *et al.*¹⁷ These observations strongly support the assignment given above for the optical absorption spectrum and the esr spectrum of the SO_3^- radical produced in the photolysis of sulfite ions.

On uv irradiation of 10^{-2} M NaHSO_3 ices in the absence of oxygen, the sample turned purple-violet and gave rise to an esr singlet shown in Figure 2b. On annealing to -75° , both the coloration and the esr signal disappeared. The color would appear to indicate that the esr singlet corresponds to the transient species with $\lambda_{\text{max}} 720 \text{ m}\mu$. However, no transients are formed on photolysis of HSO_3^- ions at room temperature, and a different esr signal was observed on uv irradiation of SO_3^{2-} ices (Figure 2a). No clear explanation is presently available to account for this observation.

Carbonate ions have been used¹⁹ to derive relative rate constants for the reaction of OH radicals with a number of solutes in the pulse radiolysis of aqueous systems. By following the decrease in optical density

(15) G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, **61**, 1674 (1965).

(16) Electron spin resonance spectra were measured by A. O. King of this laboratory.

(17) G. W. Chantry, A. Horsfield, J. R. Morton, J. R. Rowlands, and D. H. Whiffen, *Mol. Phys.*, **5**, 233 (1962).

(18) V. V. Gromov and J. R. Morton, *Can. J. Chem.*, **44**, 527 (1966).

(19) G. E. Adams and J. W. Boag, *Proc. Chem. Soc.*, 112 (1964).

at 6000 Å for the CO_3^- radical in the presence of, say, sulfite ions, the rate constant $k(\text{OH} + \text{SO}_3^{2-})$ was determined. We have added carbonate ions to nitrogen and nitrous oxide saturated $10^{-2} M$ SO_3^{2-} solutions and followed the transient at 500 mμ, at which wavelength the $\epsilon_{\text{HSO}_3^-} \ll \epsilon_{\text{CO}_3^-}$. By analysis of the decay curves and the "initial" optical densities, it was concluded that CO_3^- radicals react with SO_3^{2-} ions and that HSO_3^- reacted with either CO_3^- , and/or CO_3^{2-} ions. This is an example of the error that can be made in studying reactions of OH radicals by the above method, without an analysis of the decay rates and a complete knowledge of the absorption spectra of all the radicals produced in the system under study.

Photolysis of Thiocyanate Ions. The flash photolysis of potassium thiocyanate in aqueous solution showed the presence of a transient species, having reddish color and absorbing in the wavelength region 350–650 mμ. The intermediate formed, with a maximum at 485 mμ, was the same in the presence or absence of oxygen. At concentrations above $3\text{--}5 \times 10^{-4} M$ thiocyanate ions, a turbidity was noticeable on flashing the solution, and in 10^{-3} to $10^{-2} M$ CNS^- ions, the formation of sulfur masked the presence of transient absorbing species and gave rise to a strong smell of H_2S . All the work to be described below was carried out in $10^{-4} M$ KCNS solutions, prepared freshly just previous to photolysis.

Figure 3 shows the absorption spectrum of the radical produced on flash photolysis of $10^{-4} M$ CNS^- in nitrogen-saturated solution at pH 6.0. A weak absorption was found down to 260 mμ which appeared to have a decay rate similar to the species absorbing at 485 mμ, but due to the small optical density of the transient it was not possible to measure the decay rate with accuracy.

The transient optical spectrum observed is considered

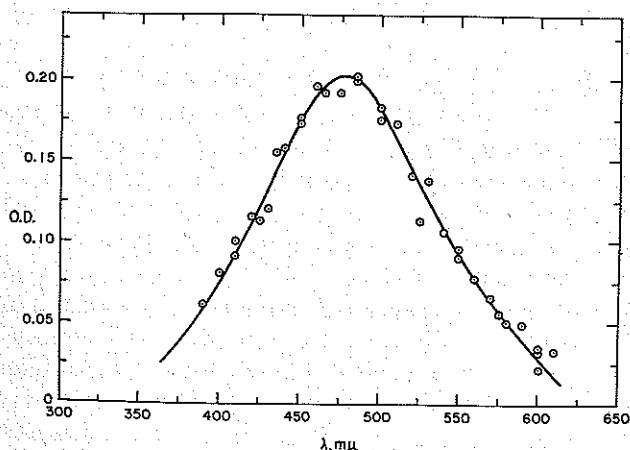
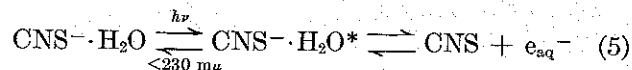
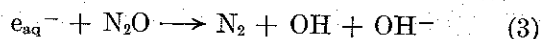


Figure 3. Transient absorption spectrum produced on flash photolysis of N_2 -saturated, $10^{-4} M$ KCNS at pH 6.0. Optical density measured in 20-cm optical cells, 80 μsec after start of flash.

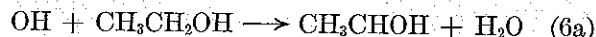
to be due to the thiocyanate radical anion, produced during the photolysis of CNS^- ions in its CTTS absorption band



While thiocyanate ions absorb light up to about 270 mμ, no transient with λ_{max} 485 mμ was formed at any $[\text{CNS}^-]$ used when a 20% acetic acid filter solution (cutoff 237 mμ) was placed between the flash tube and the optical cell. From a change in filter solutions used, it was established that the CTTS band of thiocyanate ions lies below about 2300 Å. Further support for reaction 5 was obtained on flashing a $10^{-4} M$ KCNS solution saturated with N_2O gas. Under these conditions, the initial OD at 485 mμ increased from 0.042 to 0.080, i.e., was approximately doubled. This is explained by the sequence of reactions 3 and 6.

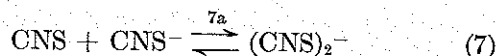


On flash photolysis of N_2O -saturated $10^{-4} M$ KCNS solution in the presence of 0.1 M ethanol, the amount of transient was the same as that produced in N_2 -saturated solutions of CNS^- and ethanol. This is explained as due to the competition between reaction 6 and



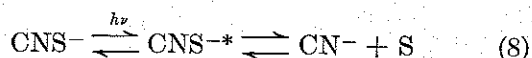
with all the OH radicals reacting with ethanol under these experimental conditions.

A similar transient has been observed in the pulse radiolysis of aqueous thiocyanate solutions²⁰ and has recently been definitely assigned to the $(\text{CNS})_2^-$ radical anion by Baxendale and Stott²¹ with $k_6 = 2 \times$



$10^{10} M^{-1} \text{sec}^{-1}$, $k_{7a} = 6.6 \times 10^9 M^{-1} \text{sec}^{-1}$, and $\epsilon_{500} = 7 \times 10^3 M^{-1} \text{cm}^{-1}$.²¹ Under our experimental conditions, it can be assumed that all the CNS radicals are present as $(\text{CNS})_2^-$.

In addition to the primary process 5, one must propose another reaction to explain the formation on photolysis (in presence or absence of acetic acid filter) of sulfur and H_2S in the system. Furthermore, this reaction must be independent of N_2O and take place in the presence of acetic acid filter; that is to say, this other photolytic process should not be limited to the CTTS wavelength band of CNS^- ions. Reaction 8 is proposed to take place. The dependence of the forma-



(20) G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael, "Pulse Radiolysis," M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Ed., Academic Press London, 1965.

(21) J. H. Baxendale and D. A. Stott, *Proc. Chem. Soc.*, 699 (1967)

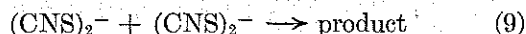
Table II: Rate Constants for the Decay of Transient Species Produced on Flash Photolysis of KCNS in Aqueous Solution

System	pH	λ , $\text{m}\mu$	Decay order	Decay rate
$10^{-4} M$, N_2 satd	6.0	480	First	$k = 3.0 \pm (1.5 \times 10^3) \text{ sec}^{-1}$
$10^{-4} M$, N_2 satd	6.0	550	First	$k = 2.5 \pm (1.0 \times 10^3) \text{ sec}^{-1}$
$2.5 \times 10^{-5} M$, N_2 satd	6.0	485	First	$k = 3.0 \pm (1.0 \times 10^3) \text{ sec}^{-1}$
$2 \times 10^{-4} M$, N_2 satd	6.0	485	First	$k = 2.8 \pm (1.2 \times 10^3) \text{ sec}^{-1}$
$10^{-4} M$, N_2 satd	0.75	485	First	$k = 2.0 \pm (1.0 \times 10^3) \text{ sec}^{-1}$
$10^{-4} M$, N_2 satd	11.9	485	Second	$2k/\epsilon = 8.9 \pm (3.0 \times 10^6)$
$10^{-4} M$, air satd	6.0	485	Second	$2k/\epsilon = 2.4 \pm (0.6 \times 10^6)$
$2.5 \times 10^{-5} M$, air satd	6.0	485	Second	$2k/\epsilon = 1.6 \pm (0.6 \times 10^6)$
$10^{-4} M$, air satd	11.9	485	Second	$2k/\epsilon = 7 \pm (2 \times 10^6)$
$(2.5-20) \times 10^{-4} M$, N_2O satd	6.0	485	First	$k = 2.0 \pm (1.0 \times 10^3) \text{ sec}^{-1}$
$10^{-4} M$, N_2O satd	11.9	485	First	$k = 2.8 \pm (0.6 \times 10^3) \text{ sec}^{-1}$
$10^{-4} M$, N_2O satd	1.0	485	First	$k = 2.6 \pm (1.0 \times 10^3) \text{ sec}^{-1}$
$10^{-4} M$, 0.1 methanol, N_2 satd	6.0	485	First	$k = 6.0 \pm (2.0 \times 10^3) \text{ sec}^{-1}$
$10^{-4} M$, 10^{-3} to $10^{-4} M$ allyl alcohol, N_2 satd	6.0	485	First	$k = 2.9 \pm (0.7 \times 10^3) \text{ sec}^{-1}$
$10^{-4} M$, $10^{-3} M$ allyl alcohol, air satd	6.0	485	First	$k = 3.7 \times 10^3 \text{ sec}^{-1}$

tion of sulfur and H_2S on CNS^- ion concentration could be explained in part due to reactions of the type $\text{S} + \text{CNS}^- \rightarrow \text{CN}^- + \text{S}_2$. Addition of allyl alcohol, a possible scavenger for sulfur, was found to reduce the initial amount of transient produced on flashing, not to affect the decay rate of the transient at 485 $\text{m}\mu$, and to essentially eliminate the turbidity caused by the formation of sulfur in reaction 7. Similar results have been found independently by Luria and Treinin.²²

The decay rate of the transient produced on photolysis of CNS^- ions in nitrogen-saturated neutral and acidic solution was found to be a fairly good first-order decay at wavelength 400–600 $\text{m}\mu$ and was found to be independent of CNS^- ion concentration from 2.5×10^{-5} to $2 \times 10^{-4} M$; see Table II. The decay could still, however, be a pseudo-first-order decay. The decay is also first order in neutral, acid, or alkaline solutions saturated with N_2O gas. In presence of oxygen, however, the decay rate is a fairly good second order with $2k/\epsilon = 2.0 \pm (0.6 \times 10^6)$. In air-saturated $10^{-4} M$ CNS^- at pH 1.0 and 1.8, decay of the transient at 485 $\text{m}\mu$ cannot be established, since it is an equally good first-order decay ($k = 4.2 \times 10^3 \text{ sec}^{-1}$).

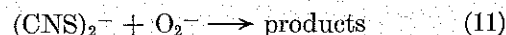
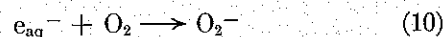
Adams, *et al.*,²⁰ have found in pulse-radiolysis work that in neutral solutions in the presence or absence of oxygen, $(\text{CNS})_2^-$ decays by a second-order process with $2k_0 = 2.9 \times 10^9 M^{-1} \text{ sec}^{-1}$, taking $\epsilon_{500} = 7.1 \times 10^3 M^{-1} \text{ cm}^{-1}$.



In acid solutions in the presence of oxygen, they found²⁰ a more complex decay kinetics for the transient absorbing at 500 $\text{m}\mu$.

No explanation is presently available to explain

the difference in decay of apparently the same species $(\text{CNS})_2^-$ produced in flash-photolysis and pulse-radiolysis experiments. The second-order decay obtained in flash photolysis in presence of oxygen could be due to the reactions



From the results obtained, it would appear that there are at least two simultaneous primary processes occurring during the photolysis of thiocyanate ions with light of wavelength above about 2000 Å: a spectroscopic excited state at $\lambda < 230 \text{ m}\mu$ originating from a CTTS transition and leading to the ejection of an electron (reaction 5), and probably a $\pi^* \leftarrow \eta$ transition involving the no-bonding electron on the sulfur atom (reaction 8).

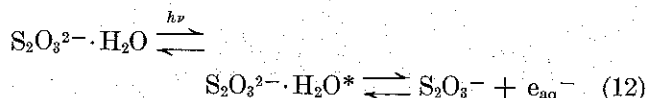
The esr spectrum of $10^{-2} M$ KCNS ices irradiated with uv light was determined and is shown in Figure 2c. The sample was found to be red on photolysis, in keeping with the expected absorption spectrum of thiocyanate radicals. On annealing to -95° the red disappeared as well as the esr absorption signal.

Photolysis of Thiosulfate Ions. The optical absorption spectra of two transient species have been observed in the flash photolysis of sodium thiosulfate in aqueous solution: a "short-lived" intermediate A absorbing in the region 340–450 $\text{m}\mu$ with $\lambda_{\text{max}} \sim 380 \text{ m}\mu$ and a "long-lived" intermediate B absorbing from about 220 $\text{m}\mu$ to 400 $\text{m}\mu$ with $\lambda_{\text{max}} \sim 280 \text{ m}\mu$ (see Figure 4). Transients A and B were shown to be formed in the pres-

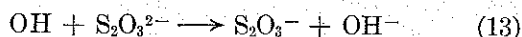
(22) M. Luria and A. Treinin, *J. Phys. Chem.*, in press.

ence or absence of oxygen and, except for variation in the amount of transients produced, at various concentrations of thiosulfate up to $10^{-2} M$ $\text{Na}_2\text{S}_2\text{O}_3$. The same transient absorption spectra were also observed in acid, neutral, and alkaline aqueous solutions. Unless stated otherwise, all the work reported below was carried out in $10^{-3} M$ $\text{Na}_2\text{S}_2\text{O}_3$ solutions.

Transient A was shown to be produced from the photoionization of thiosulfate ions and is assigned to



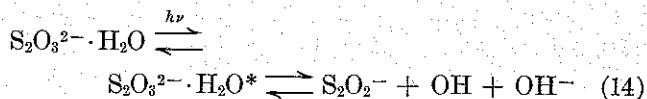
the S_2O_3^- radical anion produced by the photolysis of $\text{S}_2\text{O}_3^{2-}$ in the CTTS absorption band. On flashing a neutral $10^{-3} M$ $\text{Na}_2\text{S}_2\text{O}_3$ solution saturated with N_2O gas ($\sim 2 \times 10^{-2} M$ N_2O), the amount of transient A produced at λ 380 $m\mu$ increased by only 50% (see below) compared to a solution saturated with N_2 gas or air. The increase is due to reaction 3 followed by reaction 13 taking place. On flashing a neutral 10^{-3}



M $\text{Na}_2\text{S}_2\text{O}_3$ solutions containing up to $10^{-1} M$ ethanol in the presence or absence of $2 \times 10^{-2} M$ N_2O , the amount of transient produced was found to be decreased by about 50% compared to a N_2 - or air-saturated $\text{S}_2\text{O}_3^{2-}$ solution free of ethanol.

Transient B, with $\lambda_{\text{max}} \sim 280 m\mu$, was found to be formed by a second independent primary photolytic process. Thus it was found that whereas the optical density at 380 $m\mu$ of S_2O_3^- radical increased by $\sim 50\%$ in the presence of $2 \times 10^{-2} M$ N_2O , the optical density of transient B at 280 $m\mu$ remained the same in N_2O , N_2 , or air-saturated solutions. Furthermore, the use of filters to cut off the light output emitted from the flash lamps supports an independent mechanism leading to the formation of transient B. Use of 20% acetic acid filter (cutoff at $\sim 237 m\mu$) was found to reduce $\text{OD}_{380 m\mu}$ by about 0.5, whereas $\text{OD}_{280 m\mu}$ was reduced by 80%. Similarly, using a filter solution with a cutoff at $\sim 215 m\mu$ almost eliminated transient B but reduced transient A to about 20%. It would hence appear that the peak of the CTTS absorption band of $\text{S}_2\text{O}_3^{2-}$ ions lies mainly above 210 $m\mu$, while the absorption band giving rise to transient B is below about 215 $m\mu$. These results seem to be in agreement with the conclusions reached by Sperling and Treinin¹⁰ on their study of the electronic absorption spectrum of $\text{S}_2\text{O}_3^{2-}$ ions. They have assigned the band giving rise to transient B in this work to the allowed $\pi^* \leftarrow \eta$ transition involving the no-bonding electrons on the oxygen atoms.

It is suggested, on the basis of the results mentioned above, that transient B is the S_2O_2^- radical anion and that it is produced as a result of a break of the S-O bond in $\text{S}_2\text{O}_3^{2-}$



Reaction 14 is supported by the results mentioned above in presence of ethanol and N_2O . Thus addition of N_2O should increase the formation of S_2O_3^- by only 50% compared to N_2 -saturated solutions, since S_2O_3^- is produced in the primary reaction 12, then from reaction 14 followed by 13 and finally from reaction 3 followed by 13. Similarly, addition of ethanol removes the OH radicals produced in reaction 14 due to reaction 6a taking place. This, therefore, results in a 50% decrease in the amount of S_2O_3^- formed. It would appear that under the conditions of our experiments, the quantum yields of reactions 12 and 14 are equal within 10-20%. The radical S_2O_2^- is not produced as a result of the decay of S_2O_3^- radicals, since, as indicated above, its formation appears to be unrelated to the amount of S_2O_3^- radicals produced.

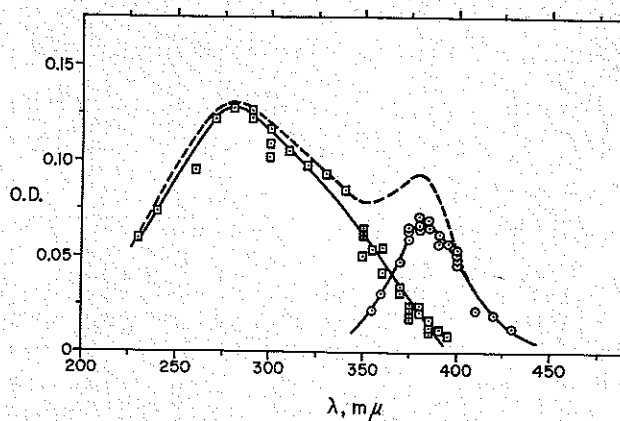
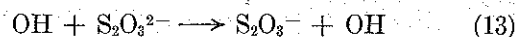


Figure 4. Transient absorption spectra produced on flash photolysis of aerated $10^{-3} M$ $\text{Na}_2\text{S}_2\text{O}_3$: —, optical density of both transients measured 100 μsec after start of flash; ○, short-lived transient S_2O_3^- measured at 100 μsec after start of flash; ◻, long-lived transient S_2O_2^- measured at 2 msec after start of flash.

Pulse-radiolysis study of aqueous solutions of thiosulfate ions was found¹⁵ to form a transient absorption with $\lambda_{\text{max}} \sim 375 m\mu$ very similar to the short-lived transient produced in the flash photolysis of $\text{S}_2\text{O}_3^{2-}$ ions and assigned to S_2O_3^- radicals. The transient observed in pulse radiolysis was shown¹⁵ to result from the reaction of OH radicals with $\text{S}_2\text{O}_3^{2-}$



and an $\epsilon_{375} = 1.72 \times 10^3 M^{-1} \text{cm}^{-1}$ was reported.

S_2O_3^- radical anions formed under flash-photolysis conditions were found to decay in neutral and alkaline solutions in the absence of oxygen by a second-order process (see Table III), with $2k/\epsilon \simeq 4 \times 10^6$ at 380 $m\mu$. Taking the value of $\epsilon_{380} = 1.72 \times 10^3 M^{-1} \text{cm}^{-1}$ reported by Adams, *et al.*,¹⁵ one obtains a value

Table III: Rate Constants for the Decay of Transient Species Produced on Flash Photolysis of $10^{-3} M \text{Na}_2\text{S}_2\text{O}_3$ in Aqueous Solution

Transient	System	pH	λ , $m\mu$	Decay order	Decay rate
S_2O_3^-	N_2 satd	Neutral	380	Second	$2k/\epsilon = 4.1 \pm (1.0 \times 10^6)$ or $2k = 7.1 \pm (1.8 \times 10^9) M^{-1} \text{sec}^{-1}$
S_2O_3^-	N_2 satd ^a	Neutral	380	Second	$2k/\epsilon = 3.7 \pm (1.0 \times 10^6)$ or $2k = 6.4 \pm (1.6 \times 10^9) M^{-1} \text{sec}^{-1}$
S_2O_3^-	Air satd	Neutral	380	First	$k = 3.0 \pm (1.5 \times 10^3) \text{sec}^{-1}$
S_2O_3^-	Air satd	Neutral	400	First	$k = 3.3 \pm (1.0 \times 10^3) \text{sec}^{-1}$
S_2O_3^-	N_2 satd	10.9	380	Second	$2k/\epsilon = 4.6 \pm (1.0 \times 10^6)$ or $2k = 7.9 \pm (2.6 \times 10^9) M^{-1} \text{sec}^{-1}$
S_2O_3^-	Air satd	10.9	380	First	$k = 2.4 \pm (1.0 \times 10^3) \text{sec}^{-1}$
S_2O_3^-	10^{-3} to $2 \times 10^{-2} M$ methanol, N_2 satd	Neutral	380	Second	$2k/\epsilon = 3.2 \pm (1.0 \times 10^6)$ or $2k = 5.5 \pm (2.0 \times 10^9) M^{-1} \text{sec}^{-1}$
S_2O_3^-	10^{-3} to $2 \times 10^{-2} M$ ethanol, air satd	Neutral	380	First	$k = 2.4 \pm (1.0 \times 10^3) \text{sec}^{-1}$
S_2O_3^-	$10^{-3} M \text{Na}_2\text{CO}_3$	Neutral	380	First	$k = 3.0 \pm (0.5 \times 10^3) \text{sec}^{-1}$
S_2O_3^-	$10^{-3} M$ allyl alcohol, N_2 satd	Neutral	380	First	$k = 2.6 \pm (1.0 \times 10^3) \text{sec}^{-1}$
S_2O_2^-	N_2 satd	Neutral	270	Second	$2k/\epsilon = 4.4 \pm (1.5 \times 10^4)$
S_2O_2^-	N_2 satd ^a	Neutral	270	Second	$2k/\epsilon = 4.0 \pm (1.5 \times 10^4)$
S_2O_2^-	Air satd	Neutral	270	Second	$2k/\epsilon = 5.7 \pm (2.0 \times 10^4)$
S_2O_2^-	N_2 satd	10.9	270	Second	$2k/\epsilon = 1.5 \pm (1.0 \times 10^5)$
S_2O_2^-	Air satd	10.9	270	Second	$2k/\epsilon = 2.0 \pm (1.5 \times 10^5)$
S_2O_2^-	10^{-3} to $10^{-1} M$ methanol, air satd	Neutral	270	Second	$2k/\epsilon = 6.0 \pm (2.0 \times 10^4)$
S_2O_2^-	10^{-3} to $10^{-1} M$ ethanol, N_2 satd	Neutral	270	Second	$2k/\epsilon = 4.0 \pm (2.0 \times 10^4)$
S_2O_2^-	$10^{-3} M$ allyl alcohol, N_2 satd	Neutral	270	Second	$2k/\epsilon = 2.0 \pm (1.0 \times 10^4)$

^a Acetic acid (20%) filter (cutoff 237 $m\mu$).

of $2k = 7.1 \pm (2.5 \times 10^9) M^{-1} \text{sec}^{-1}$. No decay order or decay rate has been reported in the pulse-radiolysis work.¹⁵ The bimolecular decay of S_2O_3^- radicals may form tetrathionate, $\text{S}_4\text{O}_6^{2-}$, a well known and relatively stable salt. In the presence of oxygen, S_2O_3^- appears to decay by a pseudo-first-order process dependent on oxygen concentration. The decay reactions taking place in presence of O_2 have not been studied in detail. Addition of ethanol, carbonate ions, or allyl alcohol does not seem to affect the decay rate of S_2O_3^- radicals; see Table III.

The S_2O_2^- transient, with $\lambda_{\text{max}} \sim 280 m\mu$, was found to decay by a second-order process, Table III, apparently independent of the presence or absence of O_2 , ethanol, and allyl alcohol.

The observation of sulfur and H_2S on flashing and the determination of these products plus sulfite ions in the photochemical decomposition of thiosulfate ions¹⁰ could, in part, result from the decay of the S_2O_2^- and S_2O_3^- radical anions. Other photolytic processes (e.g., $\text{S}_2\text{O}_3^{2-} \xrightarrow{h\nu} \text{SO}_3^- + \text{S}^-$) cannot be excluded at present. Although $k(e^- + \text{S}_2\text{O}_3^{2-}) =$

$6 \times 10^8 M^{-1} \text{sec}^{-1}$, no transient species produced from this reaction has been observed. Hydrated electrons could, however, react with thiosulfate ions to form HS^- (eventually giving H_2S) and SO_3^{2-} ions.

The esr spectrum of $10^{-2} M \text{Na}_2\text{S}_2\text{O}_3$ ices exposed to uv light was measured at 77°K and is shown in Figure 2d. The sample was yellow on photolysis, in agreement with the expected absorption spectrum of S_2O_3^- radicals. On thermal annealing to -60° , the faint yellow color, as well as the esr absorption signal, disappeared. Morton²³ has irradiated with γ rays single crystals of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and examined them with an esr spectrometer. He found the presence of two singlets due to two radicals: one brown and assigned to S_2O_2^- and the other tentatively assigned to S_2O_3^- . On the basis of the flash-photolysis results obtained above, it is suggested that the colored less stable radical observed by Morton could be due to S_2O_3^- and the more stable colorless radical to S_2O_2^- . This is exactly a reversal of the assignments given by him.

(23) J. R. Morton, *Can. J. Chem.*, **43**, 1948 (1965).